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ScienceDirect
Procedia Chemistry 1 (2009) 1553–1559
Procedia Chemistry
www.elsevier.com/locate/procedia

Boron-doped TiO_2: Characteristics and photoactivity under visible light

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Abstract

Boron-doped TiO_2 was prepared by the sol-gel method and by grinding TiO_2 powder with a boron compounds (boric acid and boric acid triethyl ester followed by calcinations at temperature range 200 to 600ºC. Three types of pristine TiO_2: ST-01 (Ishihara Sangyo Ltd., Japan; 300 m^2/g), P25 (Degussa, Germany, 50 m^2/g), A11 (Police S.A., Poland 12 m^2/g) were used in grinding procedure. The photocatalytic activity of obtained powders in visible light was estimated by measuring the decomposition rate of phenol (0.21 $mmol/dm^3$) in an aqueous solution. The photocatalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron emission spectroscopy (XPS), UV-VIS absorption and BET surface area measurements. The best photoactivity under visible light was observed for B-TiO_2 modified with 2 wt% of boron prepared by grinding ST-01 with dopant followed by calcinations at 400ºC. This photocatalyst contains 16.9 at.% of carbon and 6.6 at.% of boron in surface layer and its surface area is 192 m^2/g.

Keywords: Titanium dioxide, B-doped TiO_2, Visible light

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doi:10.1016/j.proche.2009.11.003

1. Introduction

Titanium dioxide is one of the most promising photocatalyst because of its high efficiency, low cost, chemical inertness, and long-term stability. It has been used in various fields, such as solar cells, photocatalytic splitting of water for green-energy hydrogen production, selective synthesis of organic compounds, air purification, removal of organic and inorganic pollutants, and photokilling of pathogenic organisms [1-2]. Most TiO_2 catalysts require activation by ultraviolet light because of its band gap (3.2 eV in the anatase TiO_2 crystalline phase). To improve the photocatalytic reactivity of TiO_2 and to extend its light absorption into the visible region several approaches have been proposed, such as metal-ion implanted TiO_2, reduced TiOx photocatalysts and non-metal doped -TiO_2. TiO_2 doped with N [3÷5], S [6, 7], C [8÷10] and B [11÷17] was prepared by several authors, reporting enhanced photocatalytic activity under UV or visible light.

TiO_2 nanoparticles codoped with boron precursors due to their photocatalytic capability, have received a lot of attention. Xu et al. showed that N, C and B-doped anatase TiO_2 are able to absorb visible light due to the presence of isolated impurity states in the TiO_2 band gap. [11]. Moon et al. prepared titanium–boron binary oxides by the sol–gel method. They reported that Pt-loaded Ti/B photocatalyst could decompose water into O_2 and H_2, stoichiometrically [13]. Zhao et al. reported that doping with boron and Ni_2O_3 in TiO_2 resulted in the improvement of TiO_2 in both spectral response and photocatalytic efficiency [14]. Photoactivity of B-TiO_2 nanoparticles under UV light was also investigated by Chen et al. [12]. They prepared B-doped TiO_2 with different atomic ratios of B to Ti (from 1 to 20%) by sol-gel method followed by calcination at 500 to 800ºC, using boric acid as a boron source. All B-doped TiO_2 nanoparticles calcinated at 500ºC showed higher photocatalytic activity than pure TiO_2 sample in the photocatalytic reaction of NADH regeneration under UV irradiation. Visible light driven boron doped TiO_2 was reported by us in previous work [14].

In this work, we present data regarding the influence of preparation procedure on visible light activity of boron-doped TiO_2. The powders were prepared according to two different procedures: by the sol-gel method and by grinding different kinds of anatase powders with a dopant containing boron. Boric acid triethyl ester ($(C_2H_5O)_3B$ and boric acid (H_3BO_3) were used as boron source in both catalyst preparation procedures. The effect of dopant amount, calcinations temperature and kind of TiO_2 used in grinding procedure were investigated.

2. Experimental section

2.1. Materials and instruments

Titanium (IV) isopropoxide (97%) was obtained from Aldrich Chem. Co. TiO_2 ST-01 powder having anatase crystal structure was obtained from Ishihara Sangyo, Japan. ST-01 has a specific surface area 320 m^2/g with particle size 7nm, A-11 was obtained from Z.Ch "POLICE" SA (surface area 12 m^2/g), Poland and P-25 from Degussa GmBH, Germany (surface area 50 m^2/g).. Boric acid triethyl ester (99%) and boric acid (99%) from Sigma-Aldrich Co. were used as boron source in both catalysts' preparation procedures without further purification.

Gemini V (model 2365) was used to measurements of BET surface area of the catalysts. The S_{BET} values were calculated according to the BET method using adsorption data at relative pressure p/p_o between.0.05 and 0.3.

The catalyst powder crystal structure was determined from XRD pattern measured in the range of $2Ø = 20–80^o$ using X-ray diffractometer (Xpert PRO-MPD, Philips) with Cu target Karay ($\lambda = 1.5404$ Å). The diffuse absorption spectra DRS were characterized using UV–vis spectrometer (Specord M40, Carl Zeiss) equipped with an integrating sphere accessory for diffuse reflectance.

ESCALAB-210 spectrometer (VG Scientific) was used for X-ray photoelectron spectroscopy (XPS) measurements with the Al Ka X-ray source operated at 300 W (15 kV, 20 mA). The spectrometer chamber pressurewas about 5×10^{-9} mbar. The samples were pressed into pellets before measurements. Survey spectra were recorded for all the samples in the energy range from 0 to 1350 eV with 0.4 eV step. Highresolution spectra were recorded with 0.1 eV step, 100 ms dwell time and 20 eV pass energy. 90^o take-off angle was used in all measurements. AVANTAGE data system software served for curve fitting. The background was fit using nonlinear Shirley model. Scofield sensitivity factors and measured transmission function were used for quantification. Carbon contamination C1s peak at 284.60 eV was used as reference of binding energy.

2.2. Preparation of B-TiO_2 photocatalysts

TiO_2-based catalysts were obtained according to procedures described previously [18].The procedure is presented by a simplified block diagram in Fig. 1 and 2. The resulting powders were labeled as B-E for boric acid triethyl ester and B-A for boric acid as boron precursors.

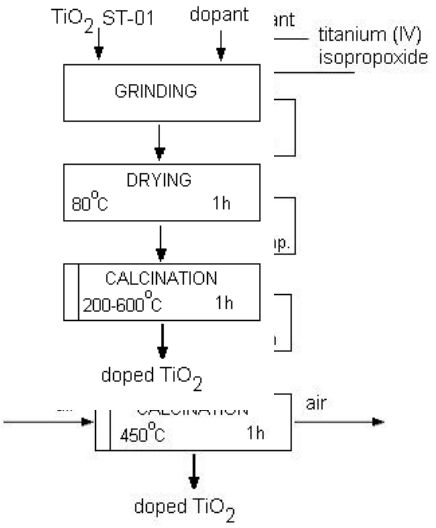

Fig 1 Block diagram of B-doped TiO_2 prepared by grinding anatase powders with dopant

Fig 2 Block diagram of B-doped TiO_2 prepared by sol-gel method.

2.3. Photocatalytic decomposition of phenol

The photocatalytic activity was estimated by measuring the decomposition rate of 0.21 mM phenol aqueous solution in Vis and UV light. Photocatalytic degradation runs were preceded with blind tests in the absence of a catalyst or illumination. Phenol was selected as a model contaminant.

25 ml of catalyst suspension (125 mg) was stirred using magnetic stirrer and aerated (5 dm^3/h) prior and during the photocatalytic process. Aliquots of 1.0 cm^3 of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters (Ø=0.2 µm) to remove catalyst particles. Phenol concentration was estimated by colorimetric method using UV-VIS spectrophotometer (DU-7, Beckman). The suspension was irradiated using 1000 W Xenon lamp (Oriel), which emits both UV and Vis light. To limit the irradiation wavelength, the light beam was passed through GG400 or UG11 filter to cut-off wavelengths shorter than 400 nm or 250 $<\lambda<$ 400 nm, respectively.

3. Results and discussion

Sample numbers and preparation conditions including kind of dopant, calcinations temperature and the amount of the dopant used during the preparation are presented in Table 1. The amount of dopant taken for catalysts preparation was calculated on the assumption that the content of boron in the catalyst after synthesis should be equal from 0.5 to 10 wt.% of the catalyst dry mass. All photocatalysts obtained by modification with boron compounds were in the form of beige powders, except BE-H(10) and BE-G(2)_350, which appeared in brownish color.

Surface properties such as surface area, band gap (E_g) and surface chemical composition together with visible light activity of obtained photocatalysts are presented in Tables 2-4. Photoactivity of obtained samples was presented as phenol decomposition rate constant, *k*. The effect of preparation method (hydrolysis or grinding) and kind of boron source on visible light activity is presented in Table 2. The highest photoactivity under visible light was observed for B-TiO_2 obtained by grinding of ST-01 with 2 wt.% of boric acid triethyl ester (k=0.0264 min^{-1}). Relevant visible light-induced activity was observed also for other samples prepared by grinding of ST-01 with boric acid triethyl ester followed by calcinations at 450ºC. All samples prepared by grinding with H_3BO_3 or by hydrolysis in the presence of boron compounds are inactive under visible light.

Measured BET surface area (see Table 2) of samples prepared by TIP hydrolysis with boric acid triethyl ester changed from 190-269 m^2/g and for samples prepared by grinding TiO_2 with boric acid triethyl ester: 2,6÷192 m^2/g. The specific surface area of pure TiO_2 obtained by TIP hydrolysis and for pure TiO_2 ST-01was 211 and 276 m^2/g, respectively. All samples, prepared by grinding ST-01 with dopant had lower surface than original TiO_2.

The band-gap was calculated from the first derivative of UV-Vis absorption spectra. For pure TiO_2 prepared by hydrolysis without any dopant, ST01, A11 and P25 the value of Eg equal 3.29; 3.27; 3.32 and 3.15 eV, respectively (see Table 4) . For TiO_2 modified with boric acid triethyl ester, Eg was in range 3.12-3.41 eV and for samples modified with boric acid fluctuated from 3.30 to3.40 eV, as presented in Table 2-4.

Carbon and boron presence in all prepared photocatalysts was confirmed by the XPS technique. Peak attributed to B1s appearing at around 192 eV and peak attributed to C 1s at around 289-284 eV. The oxidation state of B atoms incorporated in TiO_2 particles was mainly B^{3+}, as determined from the X-ray photoelectron spectra (XPS). It was confirmed that boron-doped

TiO_2 was activated by visible light and used as effective catalyst in photooxidation reactions. For B-TiO_2 series prepared by grinding of ST-01 with boric acid triethyl ester followed by calcinations at 450ºC, boron content increased from 3.21 to 12.33 at.% with increasing dopant content. To obtain information on the crystal structure of B-TiO_2 photocatalysts, X-ray diffraction patterns were measured. All samples prepared by grinding TiO_2 with boron dopant in range 0,5÷5wt.% contained anatase phase. For samples prepared with 10 wt.% of boron B_2O_3 structure was observed besides the peak due to anatase.

Table 1 Preparation condition of boron doped TiO_2

Sample No.	Type of preparation method	Kind of dopant	TiO_2 precursor	Calcination temperature [ºC]	TiO_2: dopant molar ratio	Assumed content of boron [wt. %]
BE-H(0.5)	hydrolysis	$(C_2H_5O)_3B$	TIP	450	1:0.036	0.5
BE-H(1)	hydrolysis	$(C_2H_5O)_3B$	TIP	450	1:0.072	1
BE-H(5)	hydrolysis	$(C_2H_5O)_3B$	TIP	450	1:0.36	5
BE-H(10)	hydrolysis	$(C_2H_5O)_3B$	TIP	450	1:0.72	10
BE-G(0.5)	grinding	$(C_2H_5O)_3B$	ST-01	450	1 : 0.037	0.5
BE-G(2)	grinding	$(C_2H_5O)_3B$	ST-01	450	1 : 0.148	2
BE-G(5)	grinding	$(C_2H_5O)_3B$	ST-01	450	1 : 0.37	5
BE-G(10)	grinding	$(C_2H_5O)_3B$	ST-01	450	1 : 0.74	10
BE-G(2)_200	grinding	$(C_2H_5O)_3B$	ST-01	200	1 : 0.148	2
BE-G(2)_300	grinding	$(C_2H_5O)_3B$	ST-01	300	1 : 0.148	2
BE-G(2)_350	grinding	$(C_2H_5O)_3B$	ST-01	350	1 : 0.148	2
BE-G(2)_400	grinding	$(C_2H_5O)_3B$	ST-01	400	1 : 0.148	2
BE-G(2)_450	grinding	$(C_2H_5O)_3B$	ST-01	450	1 : 0.148	2
BE-G(2)_600	grinding	$(C_2H_5O)_3B$	ST-01	600	1 : 0.148	2
BE-G(2)_A11	grinding	$(C_2H_5O)_3B$	A11	400	1 : 0.148	2
BE-G(2)_P25	grinding	$(C_2H_5O)_3B$	P-25	400	1 : 0.148	2
BA-H(0.5)	hydrolysis	H_3BO_3	TIP	450	1 : 0.04	0.5
BA-H(10)	hydrolysis	H_3BO_3	TIP	450	1 : 0.72	10
BA-G(0.5)	grinding	H_3BO_3	ST-01	450	1 : 0.04	0.5
BA-G(10)	grinding	H_3BO_3	ST-01	450	1 : 0.72	10

Table 1 Surface properties and visible light activity of boron-doped TiO_2 photocatalysts – the influence of dopant and preparation method (all sample were calcinated at 450ºC)

Sample No.	Band gap energy [eV]	BET surface area (m^2/g)	XPS-determined content [at.%]		Phenol decomposition rate constant k (min^{-1})
			C	B	
BE-H(0.5)	3.28	208	8.38	1.71	0.0034
BE-H(1)	3.37	237	8.42	1.82	0.0045
BE-H(5)	3.41	269	13.14	6.86	0.0035
BE-H(10)	3.36	190	6.92	8.66	0.0044
BE-G(0.5)	3.36	160	18.54	3.21	0.0179
BE-G(2)	3.33	176	11.89	7.6	0.0264
BE-G(5)	3.32	180	9.76	9.74	0.0116
BE-G(10)	3.37	158	18.43	12.33	0.009
BA-H(0.5)	3.34	219	19.13	1.14	0.0049
BA-H(10)	3.40	330	14.28	9.11	0.0046
BA-G(0.5)	3.30	163	10.36	2.32	0.0038
BA-G(10)	3.33	82	3.98	24.55	0.0066

Calcination temperature influence was estimated by annealing of sample BE-G(2) in the range from 200 to 600ºC. According to data presented in Table 3, the highest photoactivity under visible light was observed for B-TiO_2 obtained by calcinations at 400ºC (k=0.0287 min^{-1}).

Table 3 Surface properties and visible light activity of boron-doped TiO2 photocatalysts – the influence of calcinations temperature

Sample No.	Band gap energy [eV]	BET surface area (m^2/g)	XPS-determined content [at.%]		Phenol decomposition rate constant k (min^{-1})
			C	B	
BE-G(2)_200	3.29	180	12.58	7.97	0.0026
BE-G(2)_300	3.35	113	11.66	6.75	0.0114
BE-G(2)_350	3.37	159	18.01	5.94	0.0153
BE-G(2)_400	3.35	192	16.88	6.64	0.0287
BE-G(2)_450	3.34	183	14.43	6.53	0.0264
BE-G(2)_600	3.29	58	11.26	7.5	0.0025

After 60 min of irradiation in the presence of pure ST-01 and BE-G(2)_400 phenol was degraded in 27% and 82%, respectively. Increase of temperature to 600ºC or decrease to 200ºC cause to loss of photoactivity. Phenol decomposition rate constant was 0.0026 and 0.025 $min.^{-1}$ for samples annealed at 200 and 600ºC, respectively. Calcination temperature did not affect on boron content. Average boron content in surface layer was 6.9 at.%,.

Properties of three types of TiO_2 (A-11, P-25 and ST-01) and B-TiO_2 obtained by grinding them with 2 wt. % of boric acid triethyl ester are presented in Table 4. The most active photocatalyst (k = 0.0287 min.-1) was prepared by using ST-01 having the biggest surface area.(276 m^2/g). Photocatalyst obtained from A11 (surface area 12 m^2/g) revealed lower photoactivity (k = 0.0019 $min.^{-1}$). For photocalyst prepared by the same procedure by using various TiO_2 precursors, different boron

concentration in surface layer was observed. Sample BE-G(2)_A11, obtained from TiO_2 A11, revealed higher content of boron (11.22 at.%). Relatively high boron concentration resulted from low surface area of A11 TiO_2 (12 m^2/g).

Table 2. Surface properties and visible light activity of different nonmodified TiO_2 and boron-doped TiO_2 photocatalysts prepared by grinding of various types of TiO_2 with 2 wt. % of boric acid triethyl ester

Sample No.	Band gap energy [eV]	BET surface area (m^2/g)	XPS-determined content [at.%]		Phenol decomposition rate constant k (min^{-1})
			C	B	
BE-G(2)_A11	3.32	2.6	3.93	11.22	0.0019
BE-G(2)_P25	3.12	168	8.02	7.61	0.001
BE-G(2)_400	3.35	192	16.88	6.64	0.0287
P 25	3.15	58	-	-	0.0039
A11	3.32	12	-	-	0.002
TiO_2 ST-01	3.27	276	-	-	0.0011
Pure TiO_2	3.29	211	-	-	0.005

Sample BE-G(2)_450 was prepared independently two times (therefore in Table 5 is marked as BE-G(2)_A and BE-G(2). Both samples prepared by grinding of ST-01 with 2% of boric acid triethyl ester revealed similar photoacivity. Phenol degradation rate constant was 0.0264 min^{-1}, although surface carbon and boron content differed within 21 and 16%.

Table 3. Comparison of photoactivity and surface properties of BE-G(2) prepared independently

Sample No.	Band gap energy [eV]	BET surface area (m^2/g)	XPS-determined content [at.%]		Decomposition rate constant k (min^{-1})
			C	B	
BE-G(2)_A	3.33	176	11.89	7.6	0.0264
BE-G(2)_B	3.34	184	14.43	6.53	0.0264

Absorption properties of boron doped TiO_2 was estimated by UV-vis spectroscopy. Figure. 1 shows the absorption spectra of B-TiO_2 doped with boric acid. Since, all samples prepared by hydrolysis in the presence of H_2BO_3 were inactive in the reaction of phenol degradation under visible light, they revealed stronger absorption in visible region than pure TiO_2. From all samples the best photoabsorption can be attributed to sample BE-H(10) obtained hydrolysis of TIP in the presence of 10 wt.% of boric acid.

Figure 2 shows the absorption spectra of B-TiO_2 doped with boric acid triethyl ester prepared by grinding of ST-01 with a dopant. The best photoabsorption in the visible region can be attributed to the sample showing the higher photoactivity in the reaction of phenol degradation - BE-G(2). We did not observe a red shift for boron-doped photocatalysts but some samples show lack of sharp absorption edge as observed for pure TiO_2.

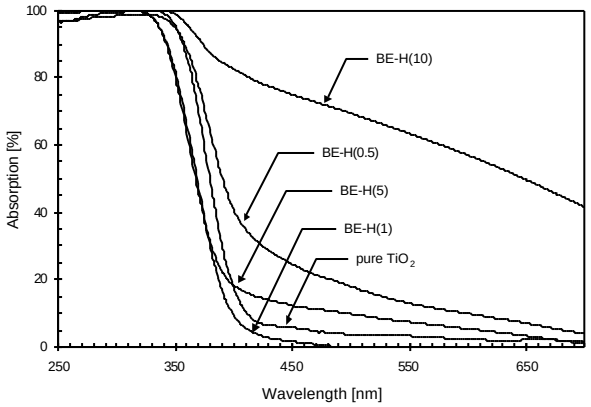

Fig. 1 Diffuse reflectance spectra of pure and B-doped prepared by hydrolysis of TIP in the presence of $(C_2H_5O)_3B$

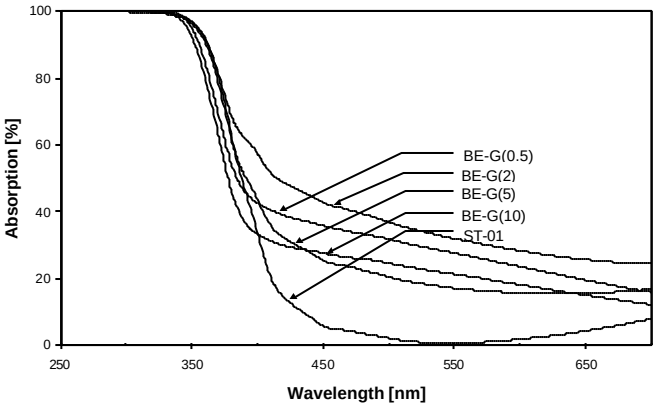

Fig. 2 Diffuse reflectance spectra of B-TiO_2 prepared by grinding anatase with different amount of $(C_2H_5O)_3B$.

4. Conclusion

All samples prepared by hydrolysis of TIP with boric acid or boric acid triethyl ester revealed similar photoactivity under vis light as pure TiO_2. Better photoactivity under visible light was observer for samples prepared by grinding TiO_2 with boric acid triethyl ester. Obtained results indicate that the amount of dopant and the temperature of calcination affected the visible light activity of boron-doped TiO_2. The best photoactivity under visible light was observed for B-TiO_2 modified with 2 wt% of boron prepared by grinding ST-01 with dopant.

Acknowledgments

Polish Ministry of Science and Higher Education is acknowledged for financial support (grant No.: N N523 483334). Dr. Beata Tryba from Department of Water Technology and Environmental Engineering, Szczecin University of Technology is gratefully acknowledged for assistance in UV-Vis spectroscopy.

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